

Coastal Groundwaters – A Geo-Hydro Chemical Exploration for Factors Controlling Genesis and Spatial Distribution of Fluoride

Mechanisms & Factors of Fluoride Genesis & Distribution

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Abstract

Fluoride being a cumulative bone seeking agent displays dual nature either, in its deficiency and/or accumulation leading to fluorosis has been a major problem along the northern districts of Bay of Bengal in Andhra Pradesh, India. Geo-hydrochemistry and mechanisms controlling fluoride genesis with its spatial distribution were delineated from 111 groundwater samples of specific criteria of two seasons. Geophysical and chemical data were interpreted with conventional and computed arguments for status, mineral species and extent along this coastal corridor of three districts. It was understood that the geo-hydrochemistry of fluoride in groundwaters is complex by virtue of the dynamic behavior of water attributed by its excellent solvent nature and the highest reactivity of fluorine. The thermodynamic equilibrium of mass transfer among ions depending on their ionic strengths by virtue of their electronic set up ultimately decided these concentrations. The variations were found to be effected with respect to the pH of the vicinity, where the dissolution or exchange of ions is enhanced or sometimes completely restricted. The correlation with respect to calcium and bicarbonates strengthen the argument of local hydro chemical and geological fluctuations from the geomorphological impacts developed from the natural and anthropogenic activities along the coast.

Key words

Bay of Bengal; Fluoride; Fluorosis; Geo-hydrochemistry; Groundwater

Introduction

Groundwaters as of universal solvent behavior are complex in their compositions with challenges from all fronts to keep their identity intact with time and space. Even though local geological factors dominate their status the seasonal and anthropogenic activities enforce the fluctuations. This is sever and continuous

in cases of coastal groundwaters with constant segregations of the elevated and the plains and intrusions of marine. Fluoride being the most important health perspective constituents of groundwater often decides the status of use for drinking. Owing to its reactivity and is therefore, never encountered in nature in the elemental form. It is seventeenth in the order of frequency of occurrence of the elements, and represents about 0.06 to 0.09% of the earth's crust [1]. Several investigators observed that the solubility of fluoride in soils is highly variable and has the tendency to be higher at pH <5 and >6 [2]. It appears that the predominant retention mechanism is that of fluoride exchange with the OH group of amorphous materials, such as Al-hydroxides. In this case, fluoride resulting in a simultaneous release of Al and Fe replaces the crystal lattice OH- of clay minerals [3, 4].

Fluoride is a typical lithophile element under terrestrial conditions and the bulk of the element is found in the constituents of silicate rocks, where the complex fluorophosphates like apatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$), seems to be one of the major fluoride minerals [5]. Next with regard to fixation of the bulk of fluoride as complex hydroxy-silicates and hydroxyaluminosilicates, in which the hydroxyl ions (OH) may be largely replaced by fluoride [6], as is the case in amphiboles and minerals of the mica family (biotite and muscovite). In many rocks, especially in those of late magmatic stages of evolution, the fluoride in such silicates may even greatly exceed the amount fixed in apatite. Not uncommonly one encounters CaF_2 as a constitution of magmatic rocks; much more rarely one finds villiaumite (NaF), in a few nepheline syenites [5]. Other fluoride retention mechanisms include the

binding of fluoride to soil cations (e.g., Ca^{2+} , Al^{3+}), or fluoride precipitation as CaF_2 , as in calcareous soils [7, 8].

It is an essential element in the following minerals: fluorite, apatite, cryolite, topaz, phlogophite, lepidolite, and other less important ones. However, micas, apatite, and tourmaline in the parent materials were the original source of fluoride in soils [9]. It appears, therefore, that the fluoride content of soils is largely dependent on the mineralogical composition of the soil's inorganic fraction. It was observed that the natural fluoride content of soil increases with increasing depth, and that only 5% to 10% of the total fluoride content of soil is water-soluble [6]. In soils of the humid temperate climate, fluoride could be-readily leach from minerals in the acid horizons. A substantial amount of this fluoride is retained in subsoil horizons, where it complexes with Al that is most likely associated with phyllosilicates [10].

Fluoride has dual significance. It helps in the normal mineralization of bones and formation of dental enamel. Fluoride when consumed in inadequate quantities (less than 0.5ppm) causes health problems like dental caries, lack of formation of dental enamel and deficiency of mineralization of bones, especially among the children. On the contrary, when fluoride consumed in excess (more than 1.0ppm), it leads to several health complications observed in all ages. Being a cumulative bone seeking mineral, the resultant skeletal changes are progressive. Higher fluoride concentration exerts a negative effect on the course of metabolic processes and an individual may suffer from skeletal fluorosis, dental fluorosis, non-skeletal manifestation or a combination of the above [11,12].

According to scientific surveys, skeletal fluorosis usually in India and China occurs when fluoride concentration in water exceeds one part per million (ppm) and was also found to occur in some communities with only 0.7 part per million [13]. Due to fluoride deficiency, the teeth lose its strength due to the decay or decrease in the dental plaque (thickness of the enamel), leading to demineralization [14]. If dental caries is affected in the front row (Canines) of the teeth it becomes a cosmetic feeling to the individual as they expose while talking or smiling, which may cause inferiority complex before others. This leads to a Psychological effect within the individual to move freely in the society thus leading in decrease of self-esteem [15]. The incidence and severity of fluorosis is related to the fluoride content in various components

of environment, viz. air, soil and water. Out of these, groundwater is the major contributor to the problem.

Groundwater quality with industrial pollutants effects was reported by Rao NS [16], temporal changes by Srinivasa Rao et. al [[17]], groundwater exploration by Das et. al [18], Fluorian allanite from calc-granulite and pegmatite contacts by Rao et. al [19], potential zones of water by Muthy et. al [20] were the existing research studies in the area. However these few studies in this area only focused on impact of industrialization with geophysical assessments and interpretations. It is evident that these studies lack the reports on concentrations of fluoride and its spatial distribution in the present study area.

In view of the importance and increasing reports of fluorosis, the present study was carried in exploring the entire coastal belt groundwaters for the assessment of fluoride levels. The geohydrochemical mechanisms controlling the genesis of fluoride and the spatial distribution in the entire area spanning over 300KM were delineated for the first time. As the onset of fluorosis is not instantaneous, its effects need time to take toll on the body and by then it would be too late neither to cure nor to prevent from further damage. The involvement of the Groundwater Board and the civil societies made the results to be disseminated in quick time in avoiding further menace of the problem and thus focus on alternatives in areas of the problem.

Study Area

The present study is a coastal corridor of three districts of Visakhapatnam, Vizianagaram and Srikakulam. Visakhapatnam district lies between $17^{\circ} 15'$ and $18^{\circ} 32'$ of Northern latitude and $18^{\circ} 54'$ and $83^{\circ} 30'$ of Eastern latitude. Vizianagaram district situated within the geographical co-ordinates of $17^{\circ} 15'$ and $19^{\circ} 15'$ of the northern latitudes and $83^{\circ} 00'$ and $83^{\circ} 45'$ of the eastern longitudes. Srikakulam district is the extreme northeastern district of Andhra Pradesh situated within the geographic co-ordinates of $18^{\circ} 20'$ and $19^{\circ} 10'$ of Northern latitude and $83^{\circ} 50'$ and $84^{\circ} 50'$ of Eastern longitude.

The area is characterized by undulating topography, with hill ranges on northern, southern and western sides, and the Bay of Bengal on the eastern side, sloping towards centrally located salt marshland from all the sides. In eastern side, the area constitutes upland, which fringes the coast and rises abruptly to form a plateau, with a height of 65–75m to mean sea

level. Eastern Ghats, which run parallel to the coast from the North-East to South-West. The slope on eastern side is towards the Bay of Bengal. The drainage system is sub-dendritic characterized by ephemeral nature. Khondalite groups (khondalites and leptynites) of the Precambrian Eastern Ghats are the geological formations, khondalites being the most dominant rocks. Charnockites, pegmatites and quartzites occur as intrusive bodies in the rocks [21]. The depth of weathered and fractured rocks is 1–18 m and 14–60 m from ground level with an average of about 11 and 35 m, respectively, depending upon the topography. The rocks are made up of quartz, feldspar, pyroxene, garnet, sillimanite, biotite, apatite and opaque of fine to coarse grained texture. The foliation trend of the rocks is NE–SW through E–W to NW–SE with a dip of 70° – 80° SE.

The main soils are red soils, sandy loams and sandy clay, which constitute 96% of the total area. The predominant soils are loamy with medium fertility. The depth of the red soil cover is up to 9m from ground surface. In some locations, laterite occurs as capping on the khondalites [21]. There are red loamy

soils in dry lands and clay loamy in wet lands. The soils at some places are as thick as 4 meters, probably represents alluvium along the valleys. Sand dunes occur along the beach. The sampling stations along the Bay of Bengal of the study area are given in Figure 1.

Criteria and Methods of Assessments

The ease and accuracy of any study or work depends largely upon the planning made prior to collection of the samples. The plan includes the location of sampling sites and parameters to be analyzed, methods of data collection and also the handling procedures. Sampling points should be such that, they represent the existing environment [22]. In the present study the procedures common as in any other studies were followed accordingly throughout and thus made the study as blend of a fresh look with typical format of experimental set up.

During the collection of a sample, care was taken in identifying the nearest possible source to the coast of a particular area and at the same time it should be a potable source for the local people. A minimum of 1 KM distance and a maximum of 2½ KM distance (depending on potable source in that area) were

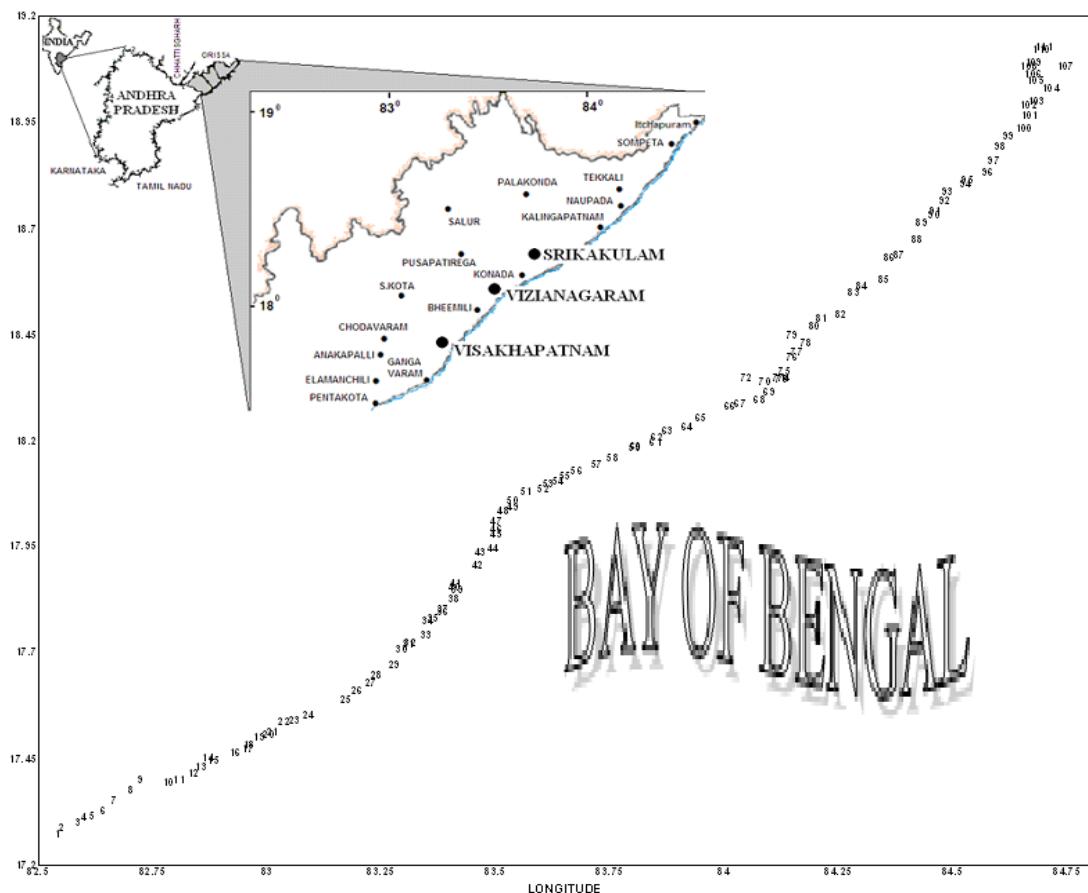


FIGURE 1 MAP OF THE STUDY AREA

maintained between the sampling stations. This provided in maintaining considerable intervals between the stations in the study area which spanned over 300 KM. In all the cases, the sample source selected was from either a community bore or open well or that of a privately owned which was obviously used by the locals as potable sources were only considered. Both the open and bore wells were included depending on their availability. Municipal sources, even in the absence of groundwater source for drinking water, in any area had not been considered for sample collection. Care was taken during the selection of open wells by neglecting the sources being monitored by the private or the Groundwater Board. By following the above mentioned criteria, samples were collected in three liter capacity polythene bottles having double stoppers.

The water samples collected were analyzed for both physical and chemical properties following the methods recommended by IS and WHO [22, 23]. For the geochemical evaluations of fluoride genesis selective parameters were analyzed involving physical and chemical characteristics. The physical characteristics include Temperature (on field), pH and the Electrical Conductance (E.C.). The chemical analysis include the estimation of the Total Dissolved Solids (TDS) and the anionic species include Carbonates (CO_3^{2-}), bi-carbonates (HCO_3^-), Chlorides (Cl^-), Fluorides (F^-), Nitrates (NO_3^-), Phosphates (PO_4^{3-}) and Sulphates (SO_4^{2-}) along with the cationic analysis is carried for the estimation of Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Sodium (Na^+) and Potassium (K^+). The district wise statistical summary was summarized in Table - 1 and in which VSP represents Visakhapatnam, VZM is for Vizianagaram and SKM is for Srikakulam district.

Results and Discussion:

The origin of high fluoride concentrations in these samples were interpreted with the help of WATEQ4F programmer [24]. It correlates an input data of the parameters given to predict the possible mineral source responsible for its existence in that particular area. The concentrations of parameters determined from the samples were recorded (geophysical and chemical constituents) in the tabular form were given as an input data file which makes the first step of the programme. Then, with a specific input file name with simultaneous output file, the programme will be executed. The WATEQ4F programmer correlates the concentrations of the parameters in their cationic and

anionic ratios with that of the existed mineral forms. Here, as all the available mineral species cationic and anionic ratios are pre-recorded, the best possible correlation will be displayed in the form of Saturation Indices.

Saturation Indices of the mineral species of an area signifies the easiness that the ions are able to leach into the groundwaters. The ionic strength of the elements constituting the mineral determines the ionic exchange in contact with the groundwaters. The difference in these strengths will initiate the process; likewise the resident time is also a key factor in leaching to the mineral species into the groundwaters. Positive S.I. values indicate a possible existence of an anion or cation in that form (mineral), whereas the negative values signify an under saturation of the form (mineral) or non-likely existence. These signify the leaching of the ions into the groundwaters.

Fluoride in the groundwaters of the present study area with health conscious can be clearly grouped into two sets. One among is the high concentrations of fluoride ($>1.5\text{ppm}$) areas observed in stations (8, 10, 14, 17, 23, 30, 42, 43, 47, 57, 77, 84, 95, 100 and 108). The samples (3, 5, 9, 11, 16, 18, 20, 24, 37, 41, 46, 49, 53, 61, 66, 71, 74, 78, 81, 88, 91, 97, 98, 101, 102, 104, 106, 109 and 110) show concentrations more than 1 ppm makes the other set. Among the three districts, Kongavani palem in Vizianagaram district bears highest concentration (2ppm).

The former set of groundwater samples come under the non-potable type as fluoride concentration crossed the permissible limit of 1.5ppm prescribed for safe drinking by World Health Organization and Indian Standards [25]. In these areas the vulnerability towards dental and skeletal fluorosis will be at its high. As far as the second set of samples which had fluoride concentration more than 1ppm, fall under the non reliable source for safe drinking, as concentrations at this rate taken as a daily dose for considerable amount of time will show its effects, especially the dental fluorosis [26]. Especially in the present study area, the young with developmental stages of teeth are more vulnerable than the old.

In evaluation of the mineral species responsible for the genesis high fluoride in the present study area the main combinations includes the concentrations of Ca^{2+} , Cl^- , PO_4^{3-} were given along with all other parameters given as input including fluoride from the analytical results of the average of pre and post monsoon seasons.

Then the WATEQ 4F programme will be run and an output file showing different Saturation Indexes (SI) values of the possible combinations of fluoride existence mineral forms such as Apatite, Fluorapatite and Fluorite in the given area will be obtained. The S.I. values of the three mineral species of fluoride in the sampling stations were tabulated in Table 2.

For the present study area the program had given the positive Saturation Index values of Apatite and negative values of Fluorite minerals. The higher the positive value, the higher possibility in existence of that mineral species in that given area. The concentrations of fluoride in the form of spatial distribution of the study area are represented in the contour map shown in fig. 2.

Even though the correlation of fluoride with Fluorite (Figure. 5) looks more positive than with of Apatite (Fig. 3) and the Fluorapatite (Fig. 4) but its negative values clearly suggests an under saturation existence of the mineral. These establish the fact that the origin of high fluoride is courtesy of former than that of the

later. The positive values observed in some cases of the Fluorapatite mineral signify the isomorphous nature of Apatite is also present in the saturation form in the study area. The dominance of Apatite over Fluorapatite (irrespective of its lower standard deviation than Apatite in their plots with fluoride) values conform its presence of the mineral in those areas of high fluoride. The reason for this would be highest electronegativity of fluoride enabling it to quickly leach upon the contact of groundwater attributes its presence in these potable waters. The probable reason for these samples' deviation from the normal trend would be theirs under saturation environment towards the new environment and sooner or later they would shift to maintain the new environment leaving the characteristics of the old environmental conditions. Another reason that would explain this deviation would be the recent changes in those areas like extension or compression between the fractures in the rocks to allow a different type of water into the formers environment and thus exhibiting variation.

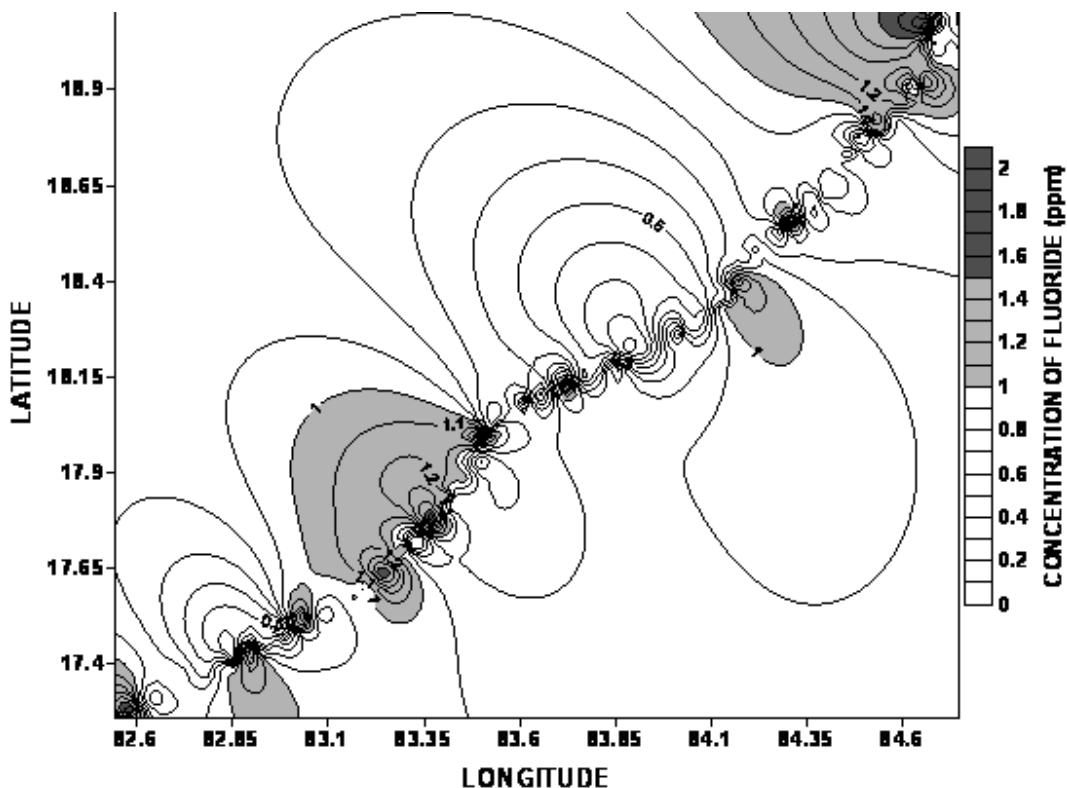


FIGURE 2 SPATIAL DISTRIBUTION OF FLUORIDE ALONG BAY OF BENGAL

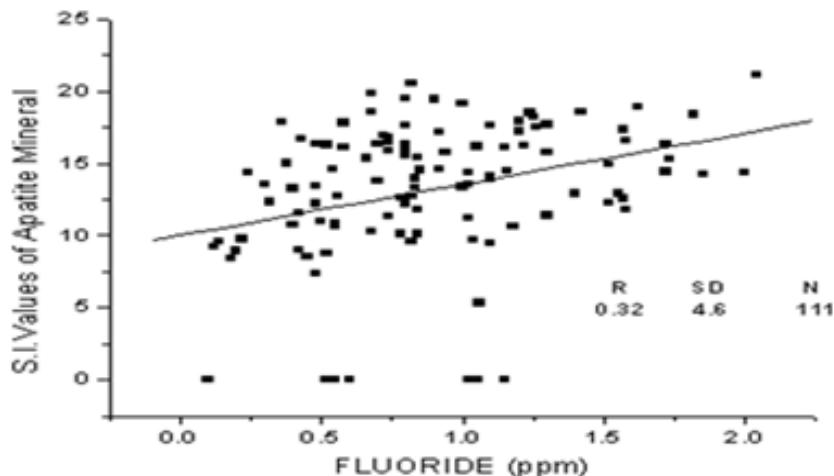


FIGURE 3 FLUORIDE VS S.I. OF APATITE MINERAL

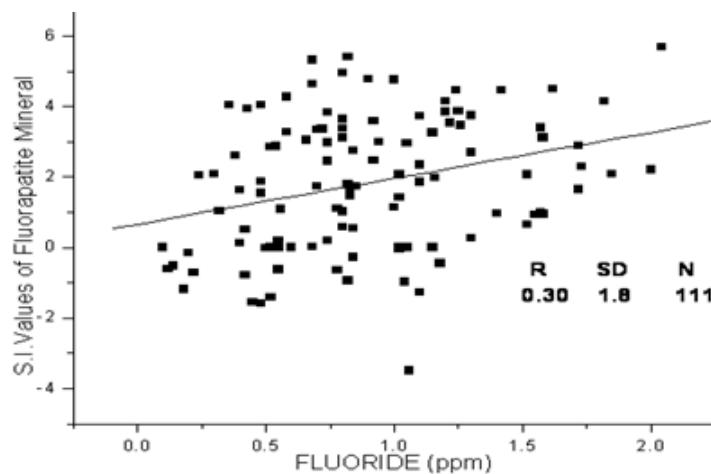


FIGURE 4 FLUORIDE VS S.I. OF APATITE MINERAL

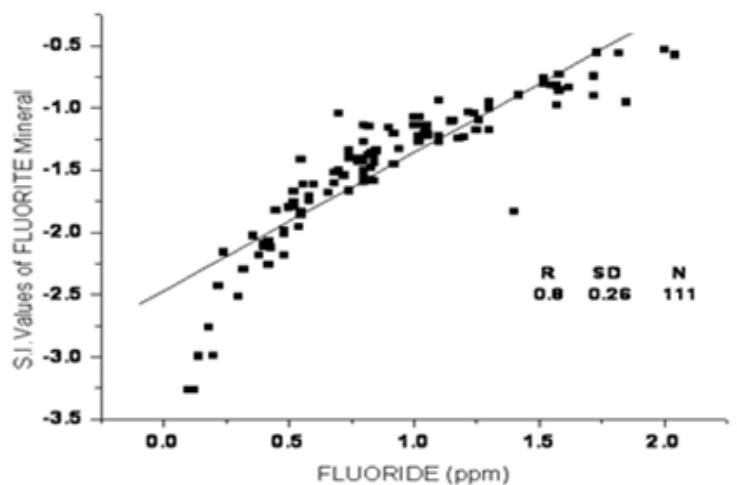


FIGURE 5 FLUORIDE VS S.I. OF APATITE MINERAL

Further confirmations of the above facts are given strength by the assessment of the ionic chemistry of the groundwaters in the present study area. The use of geochemical ratios of an area reveals the groundwater chemistry and the principle sources of the ions according to Sarin et. al [27]. According to them, the

source for the ions in the groundwaters can be predicted by using the $\text{HCO}_3^- : \text{Cl}^-$ ratio along with $\text{Ca}^{2+} + \text{Mg}^{2+} : \text{TC}$ (Total Cations) and $\text{Na}^+ + \text{K}^+ : \text{TC}$ ratios. They further stated that the cationic and anionic ratio of sodium and chloride needs to be included with the above in cases where, their percentage of contribution

in the total numbers is as significant as others. In the study area, the mean $\text{HCO}_3^- : \text{Cl}^-$ ratio was more than unity with values of 1.42 (Table 3). The $\text{Ca}^{2+} + \text{Mg}^{2+} : \text{TC}$ (Total Cations) and $\text{Na}^+ + \text{K}^+ : \text{TC}$ ratios mean values are less than unity, which are 0.39 and 0.6 respectively. With the above conditions in the study area the principal source for the chemical ions would be the rock weathering.

As the sampling sources have coastal origin, it is obvious that the sodium and chloride ratio would contribute significant information for the assessment of the source of ions in these groundwaters and there were variations in pH as well with the intrusions penetrating through the rocks to groundwater. In general, with the ratios of alkaline earths and alkalies with their total numbers showing values less than unity, their values should be more than unity in order to support the above prediction. But, the mean of sodium and chloride ratios (0.65) are less than unity in the study area. Even though there are cases which validate the criteria, the overall scenario looks quite opposite, supporting the view that rock weathering is not the only source but also other factors play their part in the genesis of the chemical ions in the groundwaters. Often the fluoride ions with their affinity to leach more than that of the chloride dominate even in minor compositions in any given area. The general trends in the overall fluorosis cases of different stages are dominant in these areas. Here also, the intrusion concentrations of the fluoride should be focused more for further segregations of the sources of fluoride in these groundwaters.

Dominance of the local variations from place to place makes groundwater chemistry change quite appreciably. This can be understood by the study of two Base Exchange Index patterns of the particular area [28]. These indexes are,

$$\text{CA}_1 = \text{Cl}^- - (\text{Na}^+ + \text{K}^+) : \text{Cl}^- \text{ and } \text{CA}_2 = \text{Cl}^- - (\text{Na}^+ + \text{K}^+) : (\text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{NO}_3^-).$$

Where CA_1 and CA_2 are Cation and Anion ratios.

When there is an exchange of Na^+ and K^+ in the groundwaters with Mg^{2+} or Ca^{2+} in the rock/weathered products (clays), both the indices will be positive. If there is a reverse exchange, then both the indexes will be negative. In the study area, mean values of the two indices are 0.3 and 0.22. In cases 24, 46, 54 and 78 the mean of both indices is negative and the rest had shown positive. In general, groundwaters with negative values of both the indices signify that the host

rocks are the primary source for dissolved ions in the area, but as in the above cases where the values obtained are positive. Moreover it can be concluded that, fluoride genesis in any coastal waters might be the geo-specific contributions rather than carried from neither the elevated nor from the plains, but it was understood that mixing of waters enhance fluoride genesis and thus indicate indirect contribution.

As the study areas lies along the coast where the groundwater flow pattern is generally altered due to the various forms of waters coming from different sources(municipal, agricultural, aqua culture, industries etc.). In the present case where most of the areas are topographically low lying and hence there is every possibility of mixing of waters from elevated zones as well. Areas like these often can have the supplement of the ions from the elevated and the plains along with that of the source rock to the groundwaters. These values are positive with values below 0.3, but at the same time the effect is not considerable. Often the seasonal variations play a great role in deciding these, as coastal waters highly suffer in maintaining their identity from widening of the intrusions during rains or from the precipitations of the ions during summers due evapotranspiration. This view can be correlated with the thoughts of Allen Zack [29] who indicated that fluoride concentrations are often found high in marine environment and adjacent coastal groundwaters are enriched.

For the evaluation of various factors that influence on the groundwater chemistry of any particular area, plots of the cationic ratio of $\text{Na}^+ : \text{Na}^+ + \text{Ca}^{2+}$ and anionic ratio of $\text{Cl}^- : \text{Cl}^- + \text{HCO}_3^-$ against TDS values were proposed by Gibbs [30]. The factors like atmospheric precipitation (rain fall), rock, pH and evaporation that govern the chemistry of groundwaters were interpreted from the plots of anionic and cationic ratios with the Total Dissolved Solids (TDS) of the study area.

The plot of $\text{Na}^+ : \text{Na}^+ + \text{Ca}^{2+}$ with TDS for the study area was given in Fig. 6a. It suggests that, along with the infiltration recharge rainwater and lithology, evaporation also plays an important role in the chemistry of the groundwaters in the area. Among them, evaporation is dominant is attributed to the marine environment close to the source. The plot of $\text{Cl}^- : \text{Cl}^- + \text{HCO}_3^-$ with that of the TDS (Fig. 6b) also show a trend remarkably similar to that for cations supporting the above prediction.

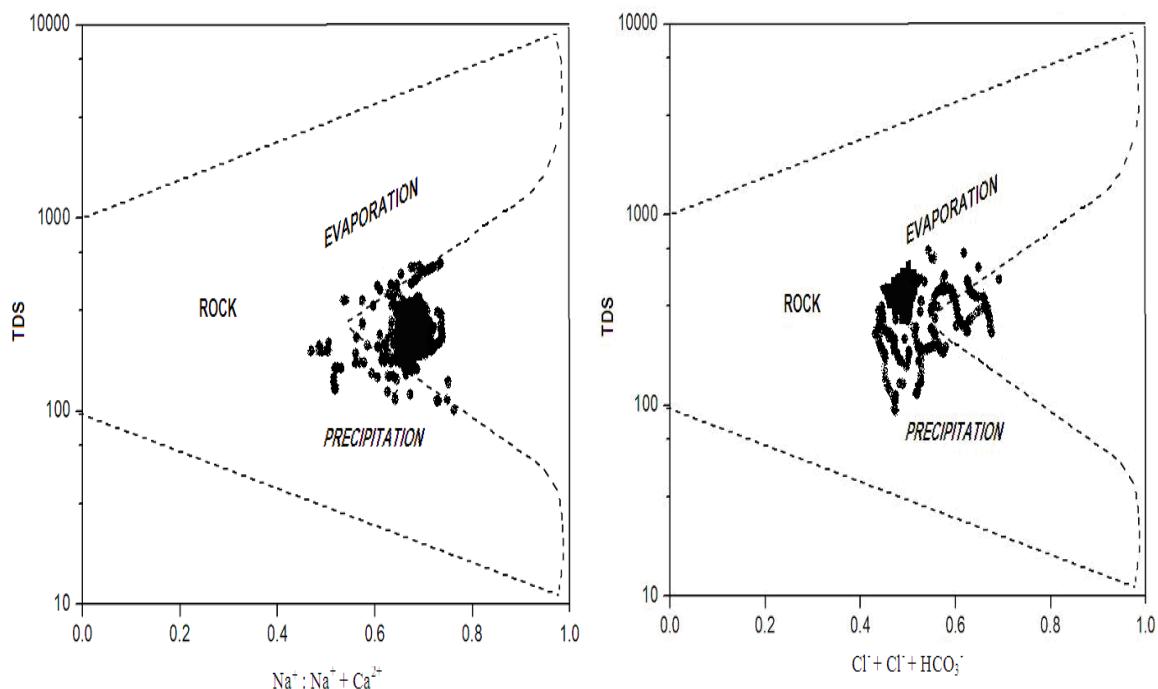


FIGURE 6 A, B MECHANISM CONTROLLING GROUNDWATER CHEMISTRY IN THE STUDY AREA

TABLE 3 HYDRO-GEOCHEMICAL RATIOS OF GROUNDWATERS ALONG BAY OF BENGAL

| Hydrogeochemical ratio | Mean |
|---|------|
| Mg ²⁺ : Ca ²⁺ | 0.90 |
| Ca ²⁺ : Mg ²⁺ : Total cations | 0.39 |
| Na ⁺ : K ⁺ : Total cations | 0.60 |
| Cl ⁻ : Na ⁺ | 1.55 |
| HCO ₃ ⁻ : Cl ⁻ | 1.42 |
| Na ⁺ : Cl ⁻ | 0.66 |
| CA ₁ = Cl ⁻ (Na ⁺ + K ⁺) : Cl ⁻ | 0.30 |
| CA ₂ = Cl ⁻ (Na ⁺ + K ⁺) : (SO ₄ ²⁻ + HCO ₃ ⁻ + CO ₃ ²⁻ + NO ₃ ⁻) | 0.22 |

Conclusions

Genesis of fluoride interpreted from the geohydrochemical mechanisms is attributed to its mineral species of apatite and its isomorphous Fluorapatite leading to different stages of fluorosis. It can also be finalized to state that in any given geological set up, the extent of fluoride depends on the amount of clayey soils and pH of the vicinity, where the pattern of fluoride distribution with depth follows clay pattern closely as observed in the areas of high fluoride. The correlations with calcium and

bicarbonates do signify the above existences for any given area. The evidence from the geochemical ratios confirming the local groundwater chemistry involving rock weathering in generating the ion in these groundwaters and mechanisms controlling these strengthen the present findings. Moreover the effects of neither the elevated nor the plains, segregating as in the present coastal area are mere qualitative and significantly deny their role in genesis of fluoride. The geology of Khondalites dominance is one of the reasons in observing these kinds of uneven variations within small vicinity of geological strata. Fluoride zones with

alternatives source maps for each district were delineated based on the observations. The timely report of these raised the consciousness in both the public and

the private for immediate initiations for alternatives. The entire data has been stored in the data bank of Groundwater Board for future needs.

TABLE 1 STATISTICAL SUMMARY OF CHEMICAL ANALYSIS DATA

| Parameter* | MINIMUM | | | MAXIMUM | | | MEAN | | | STANDARD DEVIATION | | | COEFFICIENT OF VARIATION | | |
|-------------------------------|---------|------|------|---------|------|------|--------|--------|--------|--------------------|--------|--------|--------------------------|--------|--------|
| | VSP | VZM | SKM | VSP | VZM | SKM | VSP | VZM | SKM | VSP | VZM | SKM | VSP | VZM | SKM |
| pH | 7.26 | 7.33 | 7.22 | 8.26 | 8.12 | 8.35 | 7.6 | 7.7 | 7.7 | 0.25 | 0.2 | 0.26 | 3.37 | 2.72 | 3.4 |
| E.C. | 973 | 1074 | 847 | 3053 | 2724 | 2446 | 1613.5 | 1729.1 | 1413.1 | 484.4 | 465.57 | 413.02 | 30.02 | 26.92 | 29.22 |
| TDS | 542 | 578 | 524 | 1526 | 1476 | 1674 | 996.5 | 994.23 | 942.22 | 249.4 | 271.48 | 257.58 | 25.02 | 27.3 | 27.33 |
| Ca ²⁺ | 35 | 28 | 37 | 124 | 87 | 146 | 62.54 | 56.05 | 63.7 | 20.94 | 15.06 | 18.91 | 33.48 | 26.87 | 29.69 |
| Mg ²⁺ | 23 | 29 | 21 | 92 | 82 | 115 | 55.18 | 47.23 | 52.56 | 14.75 | 13.29 | 16.52 | 26.73 | 28.15 | 31.43 |
| Na ⁺ | 89 | 83 | 85 | 322 | 302 | 386 | 176.88 | 174.88 | 172.4 | 51.92 | 65.64 | 59.25 | 29.35 | 37.53 | 34.36 |
| K ⁺ | 1 | 1 | 2 | 35 | 24 | 80 | 7.81 | 6.41 | 8.78 | 6.52 | 6.3 | 12.4 | 83.5 | 98.34 | 141.27 |
| CO ₃ ²⁻ | 0 | 0 | 0 | 40 | 20 | 40 | 4.54 | 3.52 | 3.6 | 10.44 | 7.85 | 9.63 | 229.78 | 222.67 | 267.73 |
| HC0 ₃ ⁻ | 225 | 256 | 220 | 522 | 512 | 522 | 352.95 | 343.11 | 341.8 | 67.91 | 75.2 | 69.35 | 19.24 | 21.91 | 20.28 |
| Cl ⁻ | 156 | 104 | 134 | 542 | 480 | 508 | 302.45 | 250.52 | 264.8 | 105.07 | 113.29 | 91.88 | 34.74 | 45.22 | 34.69 |
| SO ₄ ²⁻ | 19 | 16 | 19 | 102 | 89 | 124 | 43.81 | 37.58 | 42.82 | 17.83 | 19.88 | 21.08 | 40.7 | 58.96 | 48.81 |
| F ⁻ | 0.14 | 0.2 | 0.1 | 1.85 | 2 | 2.04 | 0.95 | 0.81 | 0.86 | 0.45 | 0.47 | 0.41 | 47.56 | 78.27 | 48.21 |
| NO ₃ ⁻ | 1 | 1 | 2 | 50 | 15 | 52 | 16.34 | 5.58 | 14.24 | 13.26 | 4.37 | 11.21 | 81.2 | 52.89 | 78.78 |
| PO ₄ ²⁻ | 0 | 0 | 0 | 2.07 | 1.04 | 2.55 | 0.37 | 0.22 | 0.43 | 0.46 | 0.26 | 0.58 | 126.7 | 116.55 | 133.92 |

*All parameters are expressed in ppm, except pH and E.C.; TDS = Total Dissolved Solids, E.C.= Electrical Conductivity (μ Siemens/Cm²

TABLE 2 SATURATION INDICES OF MINERAL SPECIES OF FLUORIDE ALONG BAY OF BENGAL

| Sampling station | Apatite | Fluorapatite | Fluorite | Sampling station | Apatite | Fluorapatite | Fluorite |
|-------------------------|---------|--------------|----------|-----------------------|---------|--------------|----------|
| 1. ERRAYA PALEM | 8.517 | -1.545 | -1.82 | 57. KOTAPALEM | 11.767 | 0.948 | -0.859 |
| 2. PETAPALEM | 16.951 | 3.362 | -1.542 | 58. JERRAPALEM | 13.579 | 2.071 | -2.513 |
| 3. BHEEMILI | 13.909 | 1.858 | -1.267 | 59. KUPPILI | 0 | 0 | -1.834 |
| 4. CHEPPALA UPPADA | 15.815 | 3.005 | -1.331 | 60. LAKSHMI PURAM | 16.37 | 4.033 | -1.986 |
| 5. MANGAMARI PETA | 15.812 | 2.692 | -0.955 | 61. KOYYAM | 16.118 | 3.25 | -1.114 |
| 6. DUDDUGADI METTA | 20.526 | 5.416 | -1.146 | 62. BHAGIVADAPURAM | 8.759 | -1.405 | -1.757 |
| 7. TIMMAPURAM | 12.636 | 1.101 | -1.429 | 63. DHARMAVARAM | 0 | 0 | -3.264 |
| 8. PEDA RUSHIKONDA | 12.554 | 0.999 | -0.98 | 64. BONTHALA KODURU | 9.24 | -0.609 | -3.264 |
| 9. CHINNA RUSHIKONDA | 18.544 | 4.47 | -0.897 | 65. EPPILI | 12.33 | 1.03 | -2.294 |
| 10. SAGAR NAGAR | 14.221 | 2.079 | -0.954 | 66. SRIKURAMAM | 5.329 | -3.497 | -1.22 |
| 11. JODUGULLA PALEM | 14.521 | 1.99 | -1.099 | 67. VATSAVALASA | 13.258 | 1.618 | -2.094 |
| 12. JALARIPETA | 13.483 | 1.872 | -2.01 | 68. KUNDAVANI PETA | 16.31 | 2.857 | -1.674 |
| 13. COASTAL BATTERY | 9.546 | -0.52 | -2.995 | 69. KORLAM | 16.535 | 2.973 | -1.408 |
| 14. CHINNA JALARIPETA | 16.634 | 3.118 | -0.734 | 70. VOMARAVALLI | 11.592 | 0.516 | -2.07 |
| 15. SOLDIER PETA | 12.401 | 1.017 | -1.543 | 71. MATYALESAM | 9.507 | -1.274 | -1.223 |
| 16. YARADA KONDA | 17.494 | 3.467 | -1.096 | 72. GARA | 17.851 | 4.037 | -2.027 |
| 17. DIBBAVANI PALEM | 15.293 | 2.306 | -0.556 | 73. KALINGAPATNAM-1 | 19.442 | 4.767 | -1.158 |
| 18. GANGAVARAM | 17.244 | 3.851 | -1.232 | 74. KALINGAPATNAM-2 | 18.529 | 4.462 | -1.046 |
| 19. NALLA AVA | 13.981 | 1.683 | -1.358 | 75. PEDDA PALIPETA | 0 | 0 | -1.791 |
| 20. PEDACHEPALA PALEM | 9.676 | -0.975 | -1.21 | 76. DOLA | 14.543 | 1.721 | -1.344 |
| 21. MUTYALAMMA PALEM | 15.895 | 2.45 | -1.343 | 77. DANDULAKSHMIPURAM | 14.964 | 2.064 | -0.766 |
| 22. CHEPALA PALEM | 19.527 | 4.962 | -1.141 | 78. KODURU | 0 | 0 | -1.099 |
| 23. JAGGANNA PALEM | 17.362 | 3.395 | -0.822 | 79. PRIYA AGRAHARAM | 10.102 | -0.277 | -1.585 |
| 24. KADA PALEM | 11.387 | 0.257 | -1.178 | 80. HANUMANTHAPURAM | 15.378 | 3.048 | -1.679 |
| 25. PUDIMADAKA | 9.002 | -0.789 | -2.256 | 81. BORUBADRA | 13.397 | 1.148 | -1.143 |
| 26. PALEM | 8.418 | -1.185 | -2.765 | 82. LAKKIVALASA | 17.67 | 3.643 | -1.275 |
| 27. SITA PALEM | 0 | 0 | -1.781 | 83. BHAVANAPADU | 15.034 | 2.613 | -2.183 |
| 28. LOVA PALEM | 11.315 | 0.204 | -1.395 | 84. VADDIVADA | 16.395 | 2.9 | -0.746 |
| 29. GOVINDA PALEM | 10.778 | 0.117 | -2.116 | 85. DEVUNALATADU | 10.687 | -0.624 | -1.418 |
| 30. VADA PALEM | 18.404 | 4.157 | -0.564 | 86. AMALAPADU | 11.002 | -0.011 | -1.799 |
| 31. VELPUGUNTA PALEM | 16.119 | 3.279 | -1.747 | 87. UDDANAM | 17.15 | 3.576 | -1.203 |
| 32. BANGARAMMA PALEM | 14.401 | 2.05 | -2.159 | 88. PALLIVURU | 16.197 | 2.956 | -1.155 |
| 33. KAPULAVATADA | 14.64 | 2.466 | -1.45 | 89. NAUVVLAREVU | 15.964 | 3.086 | -1.497 |
| 34. PATA POLAVARAM | 11.817 | 0.555 | -1.439 | 90. PEDDA DOKULAPADU | 16.793 | 3.831 | -1.667 |
| 35. GUDIVADA | 17.828 | 4.27 | -1.71 | 91. CHINAWAKA | 17.681 | 3.734 | -0.942 |
| 36. JANAKAYYA PETA | 12.116 | 0.592 | -1.596 | 92. BAIPILLE | 0 | 0 | -1.616 |
| 37. BOYA PADU | 0 | 0 | -1.139 | 93. AKKUPALLI | 9.763 | -0.704 | -2.433 |
| 38. DONVANI LAXMI PALEM | 10.096 | -0.638 | -1.404 | 94. MOTTURU | 15.438 | 2.74 | -1.408 |
| 39. GUNUPUDI | 12.748 | 1.088 | -1.616 | 95. PIDIMI | 12.278 | 0.655 | -0.806 |
| 40. PENTAKOTA | 13.318 | 1.452 | -1.478 | 96. RATTI | 19.891 | 5.317 | -1.521 |
| 41. GAJAPATHINAGARAM | 10.635 | -0.448 | -1.242 | 97. UPPALAM | 11.192 | -0.058 | -1.137 |
| 42. VENKATANAGARAM | 14.445 | 1.644 | -0.902 | 98. BARUVA | 12.912 | 0.962 | -1.834 |
| 43. KUMARA PURAM | 12.903 | 0.938 | -0.817 | 99. BARUVAPETA | 10.915 | 0.204 | -1.857 |
| 44. PALAMANU PETA | 13.818 | 1.744 | -1.0458 | 100. GOLLAGANDI | 18.9 | 4.5 | -0.836 |
| 45. KAVULAVADA | 12.719 | 1.795 | -1.581 | 101. MANIKYAPURAM | 17.947 | 4.153 | -1.234 |
| 46. KANCHERU | 14.147 | 2.346 | -1.274 | 102. VARAKHA | 18.188 | 3.876 | -1.177 |
| 47. KONGAVANIPALEM | 14.401 | 2.207 | -0.529 | 103. BOWRIVANKA | 9.571 | -0.937 | -1.378 |
| 48. KONADA | 12.215 | 1.537 | -1.991 | 104. KAVITI | 19.18 | 4.756 | -1.07 |
| 49. MUNJERU | 0 | 0 | -1.274 | 105. KAPASAKUDDI | 16.401 | 3.334 | -1.5 |
| 50. BHOGAPURAM | 7.367 | -1.582 | -2.18 | 106. NELAVANKA | 14.348 | 2.066 | -1.23 |
| 51. KOLLAVALASA | 10.321 | 0.011 | -1.604 | 107. BURJAPADU | 18.609 | 4.644 | -1.607 |
| 52. CHINTAPALLI | 15.533 | 3.376 | -1.568 | 108. TULASIGAM | 21.185 | 5.682 | -0.574 |
| 53. PATHIVADA | 16.262 | 3.535 | -1.038 | 109. EEDUPURAM | 17.705 | 3.742 | -1.009 |
| 54. MENTADA | 16.69 | 3.942 | -2.122 | 110. ITCHAPURAM | 13.578 | 1.408 | -1.075 |
| 55. GAJAPATHIRAJUPURAM | 8.952 | -0.157 | -2.991 | 111. ITCHAPURAM | 16.4 | 3.115 | -1.435 |
| 56. KUMILI | 14.637 | 2.869 | -1.958 | | | | |

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